Surface-State Contribution to the Electroreflectance of Noble Metals

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The effect of electromodulation of surface states on the electroreflectance of Ag(110) is investigated with use of results from a first-principles, self-consistent pseudopotential calculation of the surface electronic structure. Our model explains the polarization anisotropy observed on the (110) face of Ag, Cu, and Au. A broadening of the surface state by ~ 1 eV is explained by interactions of water dipoles at the metal-electrolyte interface.

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An intense electric field (~ 10^7 V/cm) can be applied to a metal surface in the presence of an electrolyte. The applied field is highly localized in the metal-electrolyte boundary: It is screened out within the first layer in the metal and decays rapidly inside the electrolyte. Thus measurements of the change in the optical reflectance of the system as the electric field is varied (electroreflectance) provide a sensitive probe of the electronic structure of the metal-electrolyte interface. Many experimental investigations[1-7] have been performed, especially on noble-metal electrodes. Of the various theories proposed[1,7-9] the free-electron model,[1,9] which accounts for the modulation of the free-electron concentration at the surface by the electric field, is the most successful in explaining semiquantitatively early experimental results on polycrystalline Au and Ag electrodes.[1] However, the free-electron model has a serious shortcoming in its inability to explain the polarization anisotropy of the normal-incidence electroreflectance of the (110) faces of noble metals. This anisotropy was first observed on the Ag(110) surface[2] by Furtak and Lynch and has subsequently been found on the Au(110) and Cu(110) surfaces also.[3,4] The observed effect varies with the bias potential[2] and is sensitive to adsorption on the surface.[10] Furtak and Lynch[2] attribute the anisotropy to field-assisted interband transitions; however, their model predicts that Ag should be the only electrode exhibiting this effect. Surface microstructures[3] and anisotropy of the electron mass[6] have also been invoked as causes of the observed anisotropy, but no detailed theory has yet been presented based on these mechanisms. We have performed self-consistent pseudopotential calculations of the electronic structure of the Ag(110) surface for various applied fields. From our results we find that the observed anisotropy is caused by electromodulation of surface states on the metal.

We first discuss the free-electron model using the McIntyre-Aspnes model.[11] For normal incidence, the change in reflectance $\Delta R/R$ caused by a change $\Delta\tilde{\epsilon}_2$ of the complex dielectric function of the interfacial region is given by the formula[11,12]

$$\Delta R/R = -4q\int \frac{[\epsilon_3''\Delta\epsilon_2'(z) + (\epsilon_1 - \epsilon_3')\Delta\epsilon_2''(z)]\,dz}{(\epsilon_1 - \epsilon_3')^2 + \epsilon_3''^2}, \tag{1}$$

where q is the wave vector of the incident light, $\hat{\epsilon}_3 = \epsilon_3' + i\epsilon_3''$ is the bulk metal dielectric function, ϵ_1 is the dielectric constant of the electrolyte, and $\hat{z}$ is the surface normal. The free-electron model assumes that only the free-electron (or intraband) part $\tilde{\epsilon}_{3f}$ of the metal dielectric function is modulated by the electric field at the surface; the reflectance change $\Delta R/R$ can then be expressed in terms of the induced surface-charge-density modulation $\Delta\sigma$ which can be related to the modulating cell potential. The free-electron model predicts $\Delta R/R$ to be independent of the light polarization, in contradiction to experimental observations. Other experimental evidence exists[3] which points to the necessity of including modulations in the bound electron (or interband) part of $\tilde{\epsilon}_3$. Since the electric field penetrates less than a layer into the metal, it is imperative that any considerations of modulation of interband transitions be based on the surface electronic structure. Although surface-state modulation has previously been suggested[9] as a source of electroreflectance, no detailed calculation has previously been reported.

The electrolytes and range of bias potentials in the experiments are selected such that contact adsorption of ions on the electrode is absent. In such cases, the layer of electrolyte next to the metal is composed almost exclusively of water molecules which do not interact chemically with the silver surface. Thus the electrolyte perturbs the metal only through the local electric fields produced at the surface. We have therefore calculated the electronic structure of the Ag(110) surface for different applied electric fields. The self-consistent pseudopotential method[13] employed has been successfully applied to various calculations on clean and adsorbed surface of a number of materials. The surface is simulated by periodic slabs each nine layers thick, with a separation of 9 Å between neighboring slabs. The Ag pseudopotential used was generated by fitting to the eigenvalues and wave functions of the Ag atom in a manner similar to that proposed recently by Hamann, Schlüter, and Chiang.[14] Only *s* and *p* valence electrons are treated with this potential. An independent calculation for a five-layer slab using a first-principles pseudopotential[15] including the 4*d* electrons yields the same *sp* surface-state distribution which further substantiates the applicability of our potential. The projected band structure for the Ag(110) surface is presented in Fig. 1. The black lines labeled *A* and *B* indicate the positions of two empty surface bands for zero field, located in energy gaps around the symmetry points $\bar{X}$ and $\bar{X}'$ of the surface Brillouin zone (SBZ). Self-consistent band structures were then calculated for fields corresponding to induced charge densities of ± 2.0 $\mu\text{C/cm}^2$ and + 16.7 $\mu\text{C/cm}^2$ on the surface. The surface charge is induced by the application of a periodic long-wavelength potential. Results of our self-consistent calculations show that the applied potential is rapidly screened out in the metal (see Fig. 2). Our calculated induced charge density resembles jellium results[16] when averaged parallel to the surface, but has large variations parallel to the surface due to the crystal structure which is not taken into account by the jellium model. The positions of the surface bands are very sensitive to the applied field, shifting up by 0.6 eV relative to the bulk band structure for an induced charge of 16.7 $\mu\text{C/cm}^2$ which corresponds roughly to a bias potential of 0.3–0.5 V. Thus a modulating electric field would produce significant shifts in the interband contributions involving the surface state and hence lead to a reflectance modulation.

The experimental electroreflectance spectrum for Ag is sharply peaked at 3.9 eV, which coincides with the beginning of interband transitions in the bulk. Calculation of the bulk dielectric function shows that the interband contribution at the threshold is dominated by the $L_{2'} \rightarrow L_1$ transition. On the (110) face, four of the eight equiva-

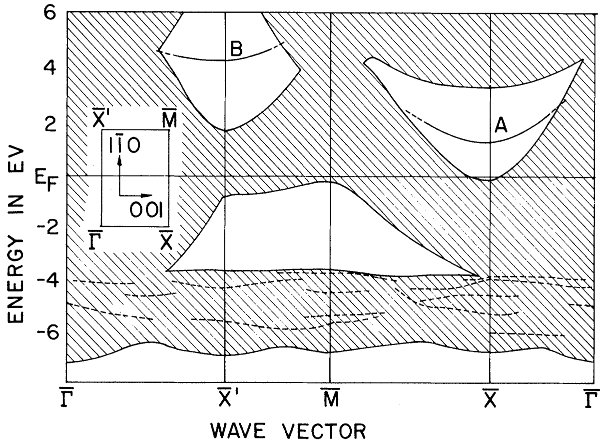

FIG. 1. The Ag(110) projected band structure together with surface states (marked *A* and *B*) and resonance bands (dashed lines). Inset shows the orientation of the SBZ with respect to the cubic crystal axes.

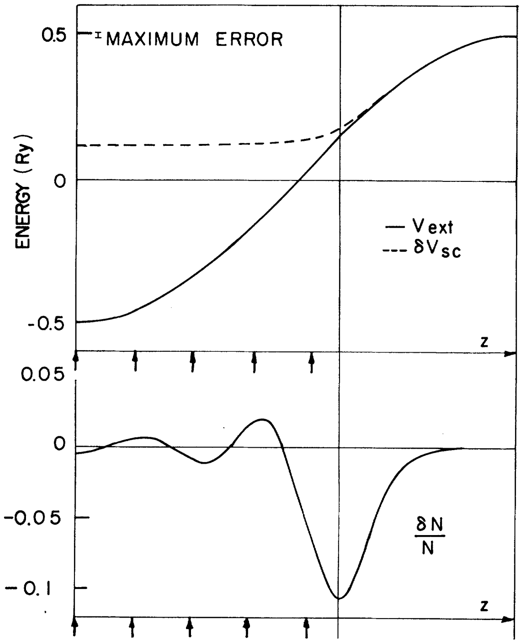

FIG. 2. The applied external potential V_{ext} and the self-consistent response δV_{sc} (top) and the induced change in electron concentration δN plotted as a function of distance perpendicular to the surface. Both δV_{sc} and δN are averaged parallel to the surface. The arrows indicate the position of atomic planes and the vertical line shows the position of the surface in the jellium model.

lent L points are projected onto the $\bar{M}$ point of the SBZ and the other four, $\pm(1,1,1)\pi/a$ and $\pm(1,1,-1)\pi/a$, project onto the $\bar{X}$ point. The gap in the projected band structure at $\bar{X}$ corresponds to the $L_{2'}\rightarrow L_1$ gap in the bulk. The surface band A comes from a band which is split down from the top of the gap and has s-like character whereas bands at the bottom of the gap which have large matrix elements with A have p-type wave functions like $\pm(x+y)+z$, $\pm(x+y)-z$. Symmetry considerations show that the optical matrix element for the transition to the surface band is zero for the $\langle 1\bar{1}0\rangle$ polarization and nonzero for the $\langle 001\rangle$ polarization. The bottom bands rise sharply above the Fermi level going away from $\bar{X}$, and thus transitions to A occur only for a small region around $\bar{X}$ and the anisotropy in the polarization dependence of the electroreflectance response follows naturally from matrix element considerations. The above arguments are verified by a calculation of matrix elements with our surface band structure.

The interband contribution can be calculated from the surface band structure:

$$\int \Delta\epsilon_{2b}\,dz = \frac{4\pi e^2}{M^2\omega^2}\int_{\mathrm{SBZ}} 2\,\frac{d^2k}{(2\pi)^2}\sum_{n,n'} f_{n\vec{k}}(1-f_{n'\vec{k}})|\langle n'\vec{k}|\vec{p}\cdot\hat{e}|n\vec{k}\rangle|^2\Delta\omega_{nn'}\frac{\partial}{\partial\omega_{nn'}}\left[\mathrm{P}\frac{2\omega_{nn'}}{\omega_{nn'}{}^2-\omega^2}+i\pi\delta(\omega_{nn'}-\omega)\right], \quad (2)$$

where $f_{n\vec{k}}$ is the occupancy of the $n\vec{k}$ state, $\hat{e}$ is the polarization vector of the light, P denotes the principal part, and $\Delta\omega_{nn'}$ indicates the shifts in the energy of the $n\rightarrow n'$ transition caused by the variation in the electric field. From our calculations we obtain the optical matrix elements, the contributing phase space, and $\Delta\omega/\Delta\sigma$ for the interband transition to the surface state. Assuming a Lorentzianlike shape for the transition, we have used Eq. (4) to evaluate the strength of the interband contribution involving the surface state A. Experimental results show that the anisotropic interband contribution and the free-electron contribution are comparable in magnitude. From this we inferred an energy width for the transition $\hbar\Gamma \sim 1.3$ eV. The spread in initial-state energy is 0.2–0.3 eV. Thus the data imply a very large width of ~ 1 eV for the surface states. This can be understood if we take into account the influence of the electrolyte. There is a distribution in the local microscopic electric field on the metal surface due to the random orientations in the adjacent water dipole layer. Using a simple electric dipole model, we have calculated the change in the local electric field when a water dipole flips and hence we are able to estimate the spread in surface-state energy caused by the disorder of water dipoles. For water-metal distances of 1.5 Å and 2 Å we obtain spreads of 2.4 and 0.9 eV, respectively, which accounts quite well for the above value of $\hbar\Gamma$.

Quantitative comparison with the observed bias-potential dependence of the electroreflectance anisotropy is difficult because of three problems: the lack of reliable experimental data for the electrode capacitance, the lack of information about possible relaxation or rearrangement of atoms at the metal surface at the interface, and the possibility of contributions from d surface states since in Ag the $d\rightarrow E_{\mathrm{F}}$ threshold lies very close (within 0.1 eV) to the $L_{2'}\rightarrow L_1$ threshold. However, some qualitative trends can be understood from our model. Near the potential of zero charge (pzc) the surface band lies at an energy below the interband threshold and no anisotropy is seen in the region around 3.9 eV. As the bias potential moves to more positive potentials the surface band is raised in energy and anisotropic contributions appear for a range of bias potentials 0.2–0.8 V above the pzc and finally disappear as either the surface band moves away from the frequency region probed or chemical reactions set in when the electrode becomes too positively biased.

Similar anisotropic features have been reported in the electroreflectance of Cu(110) and Au(110)[3-6] electrodes at frequencies close to the $L_{2'}\rightarrow L_1$ transitions. It is very probable that the same mechanism is the cause for these features as well since the band structures are all quite similar. Anisotropic features in surface reflectance spectroscopy of H on W(110) (Ref. 17) and Cu on Pt(110) (Ref. 18) have also been reported. We suspect that surface-state contributions are also present on other crystal faces. For example, a sharp feature in the electroreflectance spectrum of Au(100) is observed[5] to shift with induced surface charge at a rate very near to what is observed on Ag(110).

In conclusion, we have shown that electromodulation of metal surface states at the metal-electrolyte interface can account for the observed normal-incidence electroreflectance anisotropies on the (110) face of noble-metal electrodes. Estimates on the magnitude of the effect indicate that the surface state is broadened to a width of ~ 1 eV by interactions with water dipoles. Investigation on the effects of *d* states should give us further understanding of the electroreflectance process which shows great promise as an analytical tool for probing the metal-electrolyte interface.

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Low-Temperature ac Conductivity of Chalcogenide Glasses

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The conductivity of amorphous As$_2$Te$_3$ and As$_2$Te$_3$Ge was measured down to 4.2 K at frequencies ranging between 0.1 and 100 kHz. The ac conductivity below 100 K, which is totally unaffected by the dc conductivity, is proportional to $\omega^s T^n$ with $s = 1$ and $n \simeq 0.5$ for as-deposited films and $n \simeq 0.1$ for annealed films. These experiments are interpreted in terms of Elliott's theory based on electron pairs hopping over a barrier between both paired and random defects.

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The ac conductivity of chalcogenide glasses (As$_2$Te$_3$ and As$_2$Te$_3$Ge) has been measured for the first time at low temperatures. The power of such an experiment resides in the fact that the dc conductivity is completely removed from the measurement. This avoids the difficult problem of subtracting the dc conductivity (σ_{dc}) from the total measured conductivity to obtain the frequency-dependent conductivity [$\sigma_{ac}(\omega)$]. Indeed, this subtraction is crucially dependent on the model one assumes for the ac conductivity.[1-3] The main result of this study is that the low-temperature ($T < 100$ K) ac conductivity is proportional to $\omega^s T^n$ with $s = 1$ and $n \simeq 0.5$ for as-deposited films and $n \simeq 0.1$ for annealed films. It will be shown that this behavior is inconsistent with the quantum mechanical tunneling (QMT) theory.[4-8] On the other hand, the results can be interpreted in terms of Elliott's theory[3,9-11] which assumes correlated barrier hopping[12] (CBH) between both paired and random charged defect centers. The low-temperature measurements suggest also that the temperature dependence ($\ln\sigma \propto T$) calculated for CBH between random defect centers[3,9] does